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XX.

ON THE SEPARATION OF TITANIUM AND ALUMINUM, WITH A NOTE ON THE SEPARATION OF TITANIUM AND IRON.

By F. A. Gooch.

Communicated May 13, 1885.

In attempting to separate titanium and aluminum it is usual to resort to that method which depends upon the action of the slightly acid solution of the sulphates when submitted to prolonged boiling. The faultiness of this method, however, becomes apparent when solutions of aluminum and titanium are compared as to behavior under the conditions. To secure the complete precipitation of titanium the excess of sulphuric acid must be kept small, while to prevent the deposition of alumina the acid must be more than enough to dissolve the same amount freshly precipitated as hydrate, in the cold. Thus, upon boiling solutions containing the equivalent of 0.06 grm. of titanic oxide, 2.5 grm. of free sulphuric acid, beside alkaline sulphates, in 800 cm.^{3} of water, it was found that at the end of an hour 0.003 grm. of titanic oxide in one case, and 0.006 grm. in another experiment, had escaped precipitation; but that, when the solution of titanium had first been precipitated by ammonia and then made just acid by sulphuric acid, every trace of dissolved titanium was thrown out on boiling. The experiment, on the other hand, of boiling a gram of alum — roughly speaking 0.1 grm. of alumina — in 800 cm.^{3} of water shows almost immediately the deposition of some alumina, and the same thing happens when the alumina is first precipitated by ammonia and then dissolved by just enough sulphuric acid to effect the solution. The difficulty of so adjusting the acidity of the solution that no alumina shall be deposited and no titanium held up, is obvious. Test paper is of no aid in the case, since the reaction of alum itself and aluminic sulphate is acid. Under the circumstances it is hardly surprising that Knop* should revert from the troublesome, and only under remote conditions more exact, method of separation by boiling to the convenient but indubitably inaccurate process of parting by the use of sodic hydrate. Knop employs both the dry and the wet method, — the fusion of the oxides in sodic hydrate, and the treatment of the salts in solution with sodic hydrate in excess; but both had long before been generally discarded, and the single experiment of acidulating the alkaline filtrate from a precipitate obtained by the treatment of a pure titanium salt according to either mode, and then making alkaline with ammonia, is enough to prove their worthlessness.

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* Jahrb. f. Min. 1876, p. 756; Zeit. f. Kryst. u. Min., i. 58.

In an endeavor to secure a better means of separating titanium from aluminum I have followed two lines of experimentation; — the one based upon the observation that, under properly controlled conditions, titanium is completely precipitated and alumina held in solution when an alkaline orthophosphate, strongly acidified with formic acid, is added to the solution of salts of these elements; the other, upon the solubility of alumina and the insolubility of titanic hydrate in sufficiently strong boiling solutions of acetic acid. Two preparations of titanium were used as test material in the course of the work; — the solution of the fusion in sodic bisulphate of the hydrate precipitated by ammonia from the fluoride of titanium and potassium itself made from rutile and carefully purified by recrystallization; and the solution obtained by treating the carefully prepared double fluoride with sulphuric acid, evaporating to dryness, redissolving in sulphuric acid and diluting with water. The second mode of preparation is the better, because the amount of alkaline sulphate present in the test solution is much smaller. At first, the strength of the solution was fixed by precipitating weighed amounts by ammonia, carefully washing, igniting and weighing the precipitate; but in the course of the work it became plain that the precipitation by means of ammonic acetate, or by ammonia with the subsequent addition of acetic acid in distinct excess, yielded more precise results. On this account, therefore, the determinations of the standard of the solutions employed in the later work were made by the acetic acid process, and the determinations by ammonia were corrected to correspond. In some of the experiments bearing upon this point, the results of which are given in the figures below, precipitations by ammonia were made in the cold and the liquid then heated to boiling; in those in which acetic acid was used just in excess, this reagent succeeded the ammonia at once, and the boiling followed; when precipitation was effected in presence of large amounts of acetic or formic acid, the acid was added in the amount intended, sodic acetate in quantity more than that necessary to decompose the sulphates present was introduced, and the clear solution heated to boiling, and kept boiling for a minute or two. The acetic acid employed was the C. P. article of commerce, and contained thirty-five per cent of absolute acid. The amounts of it used — 20%, 30%, 40%, 50% by volume — correspond to 7%, 10.5%, 14%, 17.5% of absolute acid. The formic acid contained twenty-seven per cent of pure acid, and when it is said that there was in solution 5.4% of it, the absolute acid is meant; but it was the weaker acid, to the amount of 20% of the entire volume, which was actually used. The experiments were made in sets, and so appear in the record, in consequence of changes (due to slight depositions from time to time) in the strength of the test solution, which necessitated redeterminations of standard.

	Weight of Solution.	TiO_2 found.	TiO_2 in 50 grm.	Mode of Precipitation.
(1)	52.7370 grm.	0.3177 grm.	0.3012 grm.	By ammonia.
(2)	52.7610 "	0.3180 "	0.3012 "	
(3)	52.7620 "	0.3076 "	0.2912 "	By ammonia and excess of acetic acid.
(4)	41.8010 "	0.2436 "	0.2914 "	
(5)	52.9420 "	0.3381 "	0.3193 "	By ammonia.
(6)	53.0200 "	0.3384 "	0.3191 "	
(7)	10.6300 "	0.0667 "	0.3137 "	By acetic acid 7% by volume.
(8)	10.6960 "	0.0671 "	0.3137 "	
(9)	21.1030 "	0.1285 "	0.3044 "	By ammonia.
(10)	21.1480 "	0.1290 "	0.3049 "	
(11)	21.0810 "	0.1248 "	0.2960 "	By acetic acid 14% by volume.
(12)	21.1670 "	0.1259 "	0.2974 "	
(13)	21.0620 "	0.1270 "	0.3015 "	By ammonia.
(14)	21.2310 "	0.1279 "	0.3012 "	
(15)	10.4370 "	0.0617 "	0.2956 "	By acetic acid 10.5% by volume.
(16)	10.6590 "	0.0629 "	0.2950 "	
(17)	10.4870 "	0.0618 "	0.2946 "	By acetic acid 14% by volume.
(18)	10.8820 "	0.0637 "	0.2940 "	
(19)	10.4700 "	0.0615 "	0.2938 "	By formic acid 5.4% by volume.
(20)	10.7410 "	0.0627 "	0.2919 "	
(21)	52.3960 "	0.3396 "	0.3230 "	By ammonia.
(22)	52.4140 "	0.3378 "	0.3222 "	
(23)	52.6350 "	0.3340 "	0.3262 "	
(24)	52.5600 "	0.3372 "	0.3208 "	By acetic acid in distinct excess.
(25)	52.4830 "	0.3366 I " 0.3363 II "	0.3207 " 0.3204 "	
(26)	52.3700 "	0.3348 "	0.3196 "	By acetic acid 17.5% by volume.
(27)	52.6420 "	0.3374 "	0.3205 "	

It will be noticed in the examination of these figures that parallel determinations usually agree very closely. The amounts of titanic oxide indicated by those experiments in which the precipitation was made by ammonia, are much in excess of those in which acetic acid was added subsequently. Thus the difference between (1), (2) and (3), (4) amounts to more than three per cent of the total amount of the former; that between (5), (6) and (7), (8), to a little less than two per cent; that between (9), (10) and (11), (12), to about two and a half per cent; and a correction of more than two per cent must be applied to (13), (14) to bring them to correspondence with (15), (16), (17), (18). The difference between (21), (22), (23) and (24), (25), (26), (27) is about one per cent, and the smallness of this figure in comparison with the differences previously noted is apparently explicable by the fact that the solution of titanium employed in the last determinations was prepared by the second of the methods mentioned above, and carries a smaller amount of alkaline sulphate. The tendency of titanic hydrate to include the sulphates of the alkalies is not strange in view of the well-known conduct of aluminic hydrate under similar circumstances, but the amount thus held is rather surprising. The experiments in which different proportions of free acid were introduced go to show, very strikingly, that, if acetic acid exerts any solvent action whatever upon the precipitate thrown down by boiling the acetate, that action is very slight. Thus, between the mean of (24), (25) and that of (26), (27), — the one set precipitated by ammonia and treated before boiling with just a distinct excess of acetic acid, the other pair thrown out of a large volume, 700 cm.^{3}, one half of which was acid of 35% strength, by boiling, — we find a difference of but 0.0007 grm., and between the mean of (15), (16) and that of (17), (18), the difference (magnified five times by reference to 50 grm. portions) is 0.0010 grm. In (25), too, we have an experiment in which the weighed precipitate was fused in sodic carbonate, dissolved, and again precipitated as before and weighed, the two weights differing by 0.0003 grm. Moreover, the filtrates from the precipitates thrown out in presence of an excess of acetic acid, when neutralized with ammonia, failed invariably to show the smallest precipitate, and in direct experiments upon the sensitiveness of the reaction it was found that on the addition of 0.0005 grm. of titanic oxide in solution to 100 cm.^{3} of 35% acetic acid carrying a little sodic acetate a distinct precipitate appeared almost immediately on boiling. It is plain, therefore, that so far as concerns the purpose in hand the insolubility of the titanium precipitate in acetic acid may be taken as absolute. The small apparent losses to be observed in some of the determinations in which a large excess of acetic or formic acid was employed, are probably explicable by the tendency of the precipitate to change its consistency as the amount of free acid increases, and, in very acid solutions, to show an inclination to adhere in small amounts, but quite persistently, to the vessel in which precipitation takes place. The adherent precipitate may be dislodged with ease by putting a little hydrochloric acid into the beaker to which the precipitate adheres, covering and heating gently so that the acid volatilized may condense upon the walls of the beaker and again run down. By then rubbing the walls of the beaker a little and adding ammonia in excess, the trace of residual titanium is completely recovered. This method of recovery was applied in (26) and (27).

In preliminary experiments upon the first of the methods which seemed to promise a separation of titanium and aluminum, it was found that the precipitation of titanium by an alkaline orthophosphate is complete in the presence of a large amount of acetic or formic acid, and that, in the cold, and under conditions otherwise properly controlled, aluminic phosphate fails to appear. To hold up the alumina by means of acetic acid requires some care in the adjustment of the acid and phosphate, and to redissolve the precipitate once formed is a matter of considerable difficulty. Thus, to clear the solution of a precipitate produced by 1.5 grm. of the phosphate of soda and ammonia upon 0.1 grm. of alumina, it was necessary to dilute the liquid to a volume of 250 cm.^{3}, and add acetic acid until there was in the solution at least five per cent of absolute acid; and the addition of 1.5 grm. more of the precipitant again precipitated aluminic phosphate. Formic acid, however, is more active, and the balance between it and the precipitant not so delicate. When the proportion of three parts by weight of absolute formic acid to two parts of microcosmic salt is kept, the aluminic phosphate does not fall; and if, because of a deficiency of acid, precipitation does take place, the liquid immediately clears so soon as the proportion of acid and precipitant is restored. Formic acid, therefore, was used in the experiments about to be described. The test solution of titanium was that employed in the previous experiments (1) to (20), but, inasmuch as the error of the process had not yet been remarked, the standards were determined by precipitating by ammonia, and are therefore to be corrected. The application of a correction of two and a half per cent to the apparent weights of titanic oxide found by the ammonia process — the mean correction for (1), (2), (5), (6), (9), (10), (13), (14) —

cannot lead far away from the truth, since the difference between the maximum and minimum corrections observed amounts for the quantity of material employed in these experiments to but 0.0002 grm. Determinations of standard, original and corrected, are given in (28), (29), (30), and (31).

	Weight of Solution.	TiO_2 found.	Corrected TiO_2 in 50 grm.	Corrected TiO_2 in 50 cm.^{3}
(28)	52.7660 grm.	0.3867 grm.	0.3572 grm.	0.3771 grm.
(29)	52.8410 “	0.3869 “	0.3569 “	
(30)	52.5380 “	0.3810 “	0.3627 “	
(31)	52.6920 “	0.3822 “	0.3627 “	

A portion of the solution, the standard of which is set by (28) and (29), was diluted to ten times its volume, and 50 cm.^{3} of the diluted solution were used in each of the experiments immediately following. These were made to determine whether the precipitate was definite in composition, and might be weighed as such. Precipitation was effected by a solution of microcosmic salt acidified with formic acid. The precipitates of (32) and (33) were collected on paper, that of (34) on asbestos, and all were ignited and weighed directly.

	Amount taken.	TiO_2 and P_2O_5 found.	TiO_2 by Standard.	P_2O_5 by Difference.
(32)	50 cm.^{3}	0.0731 grm.	0.0377 grm.	0.0354 grm.
(33)	“	0.0640 “	0.0377 “	0.0263 “
(34)	“	0.0753 “	0.0377 “	0.0376 “

The phosphate obtained by Merz * by precipitating in presence of hydrochloric acid containing two molecules of TiO_2 to one of P_2O_5, requires 0.0326 grm. of P_2O_5 to 0.0377 grm. of TiO_2. It will be noticed that in two determinations the P_2O_5 is in a considerable excess of the amount demanded by this proportion, and in one, in deficiency. The idea of weighing the phosphoric anhydride and titanic oxide together was therefore abandoned.

In experiments (35), (36), (37), the titanium was present alone; in (38), (39), 2 grm. of alum were added to the solution before precipitating by means of the mixture of microcosmic salt and formic acid, 5 grm. of the former being employed to 8 grm. of the latter. The precipitates of all, excepting (35), were carefully washed, ignited, fused with sodic carbonate, and the product of fusion was dissolved in water, the insoluble titanate separated from the soluble phosphate

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* Jour. prakt. Chem., xcix. 157.

by filtration and washing, ignited, again fused with a little sodic carbonate, the result of fusion dissolved in strong sulphuric acid, diluted with water, and precipitated by ammonia with the subsequent addition of acetic acid, and boiling. Experiment (35) was conducted in like manner, excepting that the sodic titanate was dissolved off the filter by means of a mixture of hydrochloric and oxalic acids, the latter destroyed by potassic permanganate (since there is danger that in presence of ammonic oxalate the titanium may not be completely precipitated by ammonia), ammonia added in excess, then acetic acid to strongly acid reaction, and the liquid boiled. This mode of treating the acid titanate is not desirable, since the titanic hydrate, if precipitated but once subsequently, retains a trace of manganese. To fuse the titanate with sodic carbonate, and then treat the melt with strong sulphuric acid, is probably the best way of getting the titanium into solution again. The test solution of (28) and (29) was employed in experiment (35), and that of (30) and (31) in the rest.

From experiments (36) and (37), together with (35), which, as has been remarked, would naturally give figures slightly too high, it appears that the method indicates with accuracy the amount of titanium present. Experiments (38) and (39) indicate that the separation from alumina is not unreasonably inexact.

	Weight of Solution.	TiO_2 found.	TiO_2 by Standard.	Error.
(35)	5.2220 grm.	0.0383 grm.	0.0373 grm.	0.0010 grm. +
(36)	5.2300 "	0.0371 "	0.0370 "	0.0001 " +
(37)	5.3840 "	0.0380 "	0.0381 "	0.0001 " —
(38)	5.2920 "	0.0367 "	0.0374 "	0.0007 " —
(39)	5.2540 "	0.0383 "	0.0372 "	0.0011 " +

The tediousness of filtration, which is a consequence of the nature of the phosphate precipitate, is the great objection to the method, and on account of it the testing was pushed no further, attention being turned instead to the second line of experimentation.

The incompleteness of the precipitation of alumina by the basic acetate process in presence of a large excess of acetic acid, suggested the attempt to hold up alumina entirely by means of a sufficient excess of acetic acid while precipitating titanium. Experiments to determine the amount of acetic acid necessary to prevent the precipitation of alumina from a boiling solution of the acetate, indicate that amounts of absolute acid in excess of five per cent by volume of the solution are adequate to the purpose, and that the addition of sodic acetate in reasonable amounts does not sensibly affect conditions. It appears, further, that the addition of a very small quantity of titanium in solution to the clear boiling solution of alumina in acetic acid occasions at once a perceptible precipitation. Thus, 0.0005 grm. of titanic oxide in solution produced a distinct and appreciable opalescence in 500 cm.^{3} of liquid containing 10 grm. of alum, 15 grm. of sodic acetate (about twice the amount necessary to convert the sulphate of alumina to the acetate), and seven per cent by volume of absolute acetic acid.

In respect to holding up alumina, formic acid acts like acetic acid, but more potently.

In the following experiments to test the method quantitatively, two solutions of titanium were employed; — in (40) and (41), the solution the value of which was fixed by (15) to (18); in (42) to (46), the solution whose standard was set by (24) to (27). To the cold solution of titanium containing a little free sulphuric acid together with some alkaline sulphate were added 5 grm. of alum (approximately 0.5 grm. of alumina), 20 grm. of sodic acetate, which was always more than enough to effect the entire conversion of the aluminic and titanic sulphates to acetates, acetic acid to such amount that in experiments (42), (43), (44) there should be in the solution seven per cent by volume of absolute acid, and in the remaining experiments ten and a half per cent by volume, and water to make the entire volume 250 cm.^{3} in (40) and (41), and 400 cm.^{3} in the rest. The clear solutions obtained in this manner were raised quickly to boiling, kept at that point for a minute, and removed from over the burner so that the precipitate might settle, — as it does almost immediately. The supernatant liquid was decanted upon a filter sufficiently porous to permit very rapid filtration,* and the precipitate added immediately thereafter, and washed with 7% acetic acid followed finally by hot water. The washed precipitate was dried, ignited, and weighed. The precipitate once upon the filter and drained becomes more compact and easily washed, and strong ignition of fifteen or twenty minutes over a good Bunsen burner, after the paper is thoroughly ashed, reduces it to a weight which neither the blast-lamp nor ignition in an atmosphere of ammonic carbonate changes.

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* The paper No. 589 of Schleicher and Schüll is excellent for the purpose.

	Weight of Solution.	TiO_2 found.	TiO_2 by Standard.	Error.
(40)	10.4910 grm.	0.0645 grm.	0.0618 grm.	0.0027 grm. +
(41)	10.5970 "	0.0656 "	0.0624 "	0.0032 " +
(42)	20.9520 "	0.1450 "	0.1343 "	0.0107 " +
(43)	21.1750 "	0.1439 "	0.1357 "	0.0082 " +
(44)	21.0250 "	0.1431 "	0.1347 "	0.0084 " +
(45)	20.8740 "	0.1393 "	0.1338 "	0.0055 " +
(46)	21.0570 "	0.1402 "	0.1349 "	0.0053 " +

It is quite obvious that a single precipitation by the method used does not yield titanic oxide free from alumina. The weighed precipitate of each experiment was therefore fused with a small quantity of sodic carbonate, and the product of fusion treated in the crucible with strong sulphuric acid, which gradually with the aid of gentle heat dissolved everything completely. This solution after cooling was poured directly into 100 cm.^{3} of cold water, and, the liquid remaining clear, ammonia was added just to alkalinity, and then dilute sulphuric acid corresponding to 2.5 grm. of pure acid. The precipitate thrown down by ammonia was gradually, but after a few minutes entirely redissolved, acetic acid was added until it amounted in terms of absolute acid to ten and a half per cent of the entire volume, 20 grm. of sodic acetate introduced, the solution boiled, and the precipitate treated as previously described. The results of this second treatment are given below.

	Weight of Solution.	TiO_2 found (II).	TiO_2 by Standard.	Error.
(40)	10.4910 grm.	0.0624 grm.	0.0618 grm.	0.0006 grm. +
(41)	10.5970 "	0.0623 "	0.0624 "	0.0001 " —
(42)	20.9520 "	0.1373 "	0.1343 "	0.0030 " +
(43)	21.1750 "	0.1385 "	0.1357 "	0.0028 " +
(44)	21.0250 "	0.1369 "	0.1347 "	0.0022 " +
(45)	20.8740 "	0.1357 "	0.1338 "	0.0019 " +
(46)	21.0570 "	0.1383 "	0.1349 "	0.0034 " +

In experiments (40) and (41), in which comparatively small amounts of titanium were employed, the separation from alumina was reasonably good after the second precipitation, but in (42) to (46) the larger quantities of titanic oxide still retained notable amounts of alumina. The precipitates of (45) and (46) were, therefore, treated again just as before, to determine the effect of a third precipitation.

	Weight of Solution.	TiO_2 found (III).	TiO_2 by Standard.	Error.
(45)	20.8740 grm.	0.1347 grm.	0.1338 grm.	0.0009 grm. +
(46)	21.0570 "	0.1360 "	0.1349 "	0.0011 " +

Three precipitations left the titanic oxide of these experiments nearly free from alumina, but three such treatments involve a good deal of labor, and, moreover, it is evident that the precipitate still holds with tenacity traces of alumina. The experiment of attempting to remove residual alumina after a single precipitation, by treating the product of fusion of the precipitate in sodic carbonate with boiling water, filtering, igniting the residue, again fusing with a little sodic carbonate, and proceeding from this point to dissolve in sulphuric acid and precipitate once more as before, was therefore tried, and the result is given in the record of (47) to (50).

	Weight of Solution.	TiO_2 found.	TiO_2 by Standard.	Error.
(47)	20.8640 grm.	0.1329 grm.	0.1337 grm.	0.0008 grm. —
(48)	21.1100 "	0.1345 "	0.1354 "	0.0009 " —
(49)	20.9100 "	0.1332 "	0.1340 "	0.0008 " —
(50)	21.0020 "	0.1348 "	0.1346 "	0.0002 " +

This mode of treatment appears to remove the last traces of alumina, and yields a reasonably good separation.

It appears therefore, to recapitulate, that for the separation of titanium and aluminum either of the processes set forth in the preceding work may serve. The first, however, — which is, in brief, the treatment of the solution containing salts of the elements in question with a mixture of microcosmic salt and formic acid, in the proportion of two to three by weight, together with enough ammonic formate to take up the stronger acids, fusing the precipitate in sodic carbonate, extracting with water, fusing the residue in a small amount of sodic carbonate, dissolving in sulphuric acid and precipitating by ammonia with the subsequent addition of acetic, and boiling, — though probably fairly accurate, is, on account of the nature of the precipitated phosphate, not comparable with the second method in point of convenience. The latter process, which involves many different manipulations, — the introduction into the solution of titanium and aluminum of enough acetic acid to make from seven to eleven per cent by volume of the absolute acid, together with sufficient sodic acetate to fix all of the stronger acids in sodium salts, boiling, filtering, and washing with acetic acid of seven per cent strength, fusing the ignited precipitate in sodic carbonate, extracting with boiling water, again fusing the residue with a little sodic carbonate, dissolving in strong sulphuric acid and pouring this solution into water, neutralizing with ammonia, redissolving the precipitate in a known amount of sulphuric acid, and precipitating finally by boiling with acetic acid and sodic acetate as at first, — and appears in the description to be long and tedious, may in reality be carried out with ease and rapidity, the operations being generally short and not of a difficult nature.

In most cases in which titanium is to be separated from aluminum, it is necessary to effect the removal of iron as well. Some experiments looking to the separation of titanium and iron, by boiling the acetates in presence of a large excess of acetic acid, were unsuccessful; for, though an excess of acetic acid amounting to eleven per cent of absolute acid in the solution is enough to prevent the deposition of a basic ferric acetate, it appears, unexpectedly, that in presence of ferric acetate in solution the titanium shows a very marked tendency to remain dissolved. Thus, an amount of iron alum the equivalent of 0.2 grm. of ferric oxide, together with 10 grm. of sodic acetate and seventeen per cent of absolute acetic acid, in a total volume of 400 cm.^{3}, held 0.06 grm. of titanic oxide completely in solution during boiling prolonged a quarter of an hour. In an experiment the counterpart of this, excepting only the addition of sodic acetate, the titanium began to deposit at once on boiling; and Streit and Franz,* in proposing the ebullition of the sulphates in presence of a large excess of acetic acid as a means of procuring titanic oxide free from iron, claim a complete precipitation under these conditions. The behavior of the sulphates of titanium and zirconium when in solution together appears to be analogous to this action of the acetates of iron and titanium, and iron in the ferric condition is generally supposed to influence somewhat the precipitation of titanium from the solution of the sulphates.

When iron and titanium appear together in solution, and are to be separated, the choice lies between Stromeyer's application of Chancel's hyposulphite method,† which yields milky filtrates, — always undesirable, — and that process which involves the precipitation of iron by ammonic sulphide in presence of ammonic tartrate to hold up the hydrates which would be precipitated in its absence. This latter method has been regarded as an undesirable one chiefly on account of the inconvenience involved in the evaporation of the filtrate from the ferrous sulphide and the ignition of the residue to remove the tartaric acid, and so to permit the recovery of bases. The difficulty in question may be obviated, however, by destroying the tartaric acid by potassic permanganate added gradually to the hot solution containing enough free sulphuric acid to leave some excess after the conversion of all the permanganate. The oxidation of tartaric acid by potassic permanganate does not, as is well known, yield carbonic acid and water alone, but gives rise also to a considerable quantity of formic acid as an intermediate product. When the permanganate begins to act upon the formic acid, the oxidation, going more slowly, results in the deposition of a brown manganic hydrate, which, if any tartaric acid remains in solution, redissolves quite rapidly, and, in presence of formic acid as the only reducing agent, more slowly. When, therefore, manganic hydrate is abundantly precipitated in the boiling solution, and does not perceptibly dissolve, it is quite certain that the conversion of the tartaric acid to formic acid — which is all that is needed in this case — has been accomplished; but for the sake of greater security the addition of permanganate may be continued until its color shows in the solution. It is well, however, to make use in this process of a known amount of tartaric acid, — experience has shown that an amount equal to three times the weight of the oxides to be held in solution is sufficient, unless ammonia be used in enormous excess and the boiling prolonged, — and to employ for its destruction two and a half times its own weight of potassic permanganate, this quantity being more than enough to carry the oxidation to the final products, providing there were no deposition of manganic hydrate. The manganese thus introduced into the solution may be removed by two acetate precipitations, which, if alumina is to be separated, must be made at any rate, even if no manganese be present.

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* Jour. prakt. Chem., cviii. 65.

† Ann. Ch. Pharm., cxiii. 127.

To separate titanium, aluminum, and iron, therefore, I find it most convenient to precipitate the iron by passing hydric sulphide into the faintly ammoniacal solution of the oxides in ammonic tartrate, taking care that the solution is still ammoniacal just before filtering; to destroy the tartaric acid in the filtrate, after acidifying and boiling off the hydric sulphide by means of potassic permanganate in the manner just described, redissolving residual manganic hydrate by the addition of a little ammonic bisulphite and boiling off the excess of sulphurous acid; and to separate the titanium and aluminum by the acetate process.

A single point in the analysis of silicates may be worthy of note in this connection. If phosphoric acid be present, as is often the case, the separation of titanium from silica by the action of cold water upon the product of fusion in sodic or potassic bisulphate is liable to uncertainty, on account of the formation of the insoluble titanic phosphate which remains partly with the silica and in part clouds the filtrate. The siliceous residue should, therefore, be treated with sulphuric and hydrofluoric acids to recover titanium which may be with the silica. It is better in most cases to effect the decomposition of a silicate by means of one of the fluoride methods, or by fusion in an alkaline carbonate, the melt in the latter case being acidified with hydrochloric acid, and the residue after evaporation and filtration worked over with sulphuric and hydrofluoric acids for the recovery of that portion of the titanium which remains insoluble after the evaporation.